Operation temperature, materials and reversibility of fuel cells - electrolyser cells

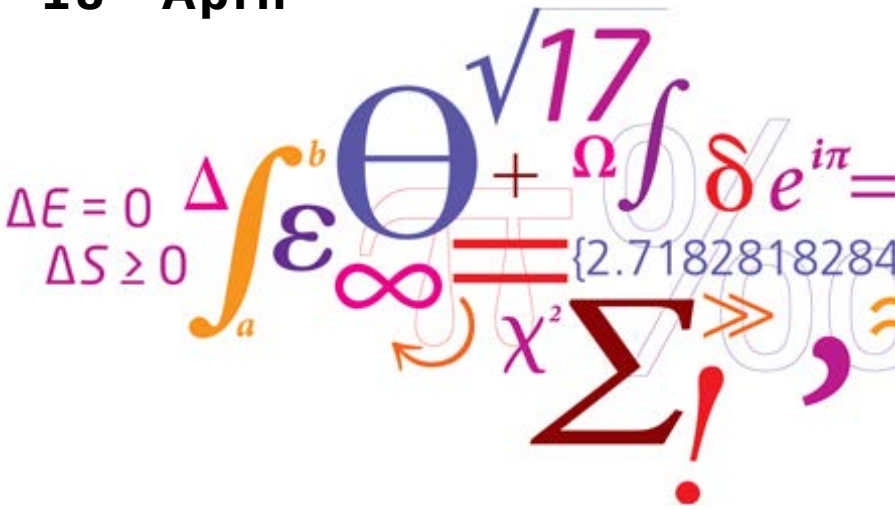
Mogensen, Mogens Bjerg

Publication date:
2013

Operation temperature, materials and reversibility of fuel cells - electrolyser cells

5th International Conference on Fundamentals & Developments of Fuel Cells, 16th – 18th April 2013, Karlsruhe, Germany

Mogens B. Mogensen



DTU Energy Conversion
Department of Energy Conversion and Storage

Outline

1. Introduction – motivation
2. Potential availability of renewable energy
3. Electrolysis is necessary
4. Vision
5. Thermodynamics
6. Types and status of electrolyzers
7. Electrocatalysis – materials - pros and cons
8. Concluding remarks

Introduction

There are clear reasons to look for means of promoting fluctuating renewable energy, e.g. photovoltaics and wind turbines:

- **Probable anthropogenic climate change by CO_2 emissions**
- **Limited supply of cheap fossil fuel resources in the long term**
- **Security of supply and geopolitical consequences of unequal distribution of resources**

Synthetic fuels – CO_2 neutral green fuels - seem particularly benign to replace the fossil fuels.

We show that this reveals great perspectives of electrolysis and CO_2-recycling for production of sustainable and CO_2 neutral energy

What to do? – The Danish answer

- **Denmark aims to become independent of fossil fuel by 2050.**

  Energy strategy 2050 - from coal, oil and gas to green energy, The Danish Government, February 2011, http://www.ens.dk/Documents/Netboghandel%20-%20publikationer/2011/Energy_Strategy_2050.pdf

- **Natural to look for photosynthesis products (biomass), but not enough biomass**

  H. Wenzel, "Breaking the biomass bottleneck of the fossil free society", Version 1, September 22nd, 2010, CONCITO, http://www.concito.info/en/udgivelser.php

Enough renewable energy

- **Yes, fortunately, enough is potentially available.**

- **The annual global influx from sun is ca. 3 - 4·10^{24} J - marketed energy consumption is ca. 5·10^{20} J;**

  References.:

  1)A. Evans et al., in: Proc. Photovoltaics 2010, H. Tanaka, K. Yamashita, Eds., p. 109.

  2) Earth's energy budget, Wikipedia, http://en.wikipedia.org/wiki/Earth's_energy_budget.

  3) International Energy Outlook 2010, DOE/EIA-0484(2010), U.S. Energy Information Administration, http://www.eia.gov/oiaf/ieo/index.html

- **Earth's surface receives at least ca. 6 - 8,000 times more energy than we need. In deserts, intensity is higher than average at the same latitude – dry air**

- **If 0.2 % of the earth's area (ca. 1 mill. km^2 or 15 % of Australia) and if collection efficiency = 10 %, we get enough energy.**

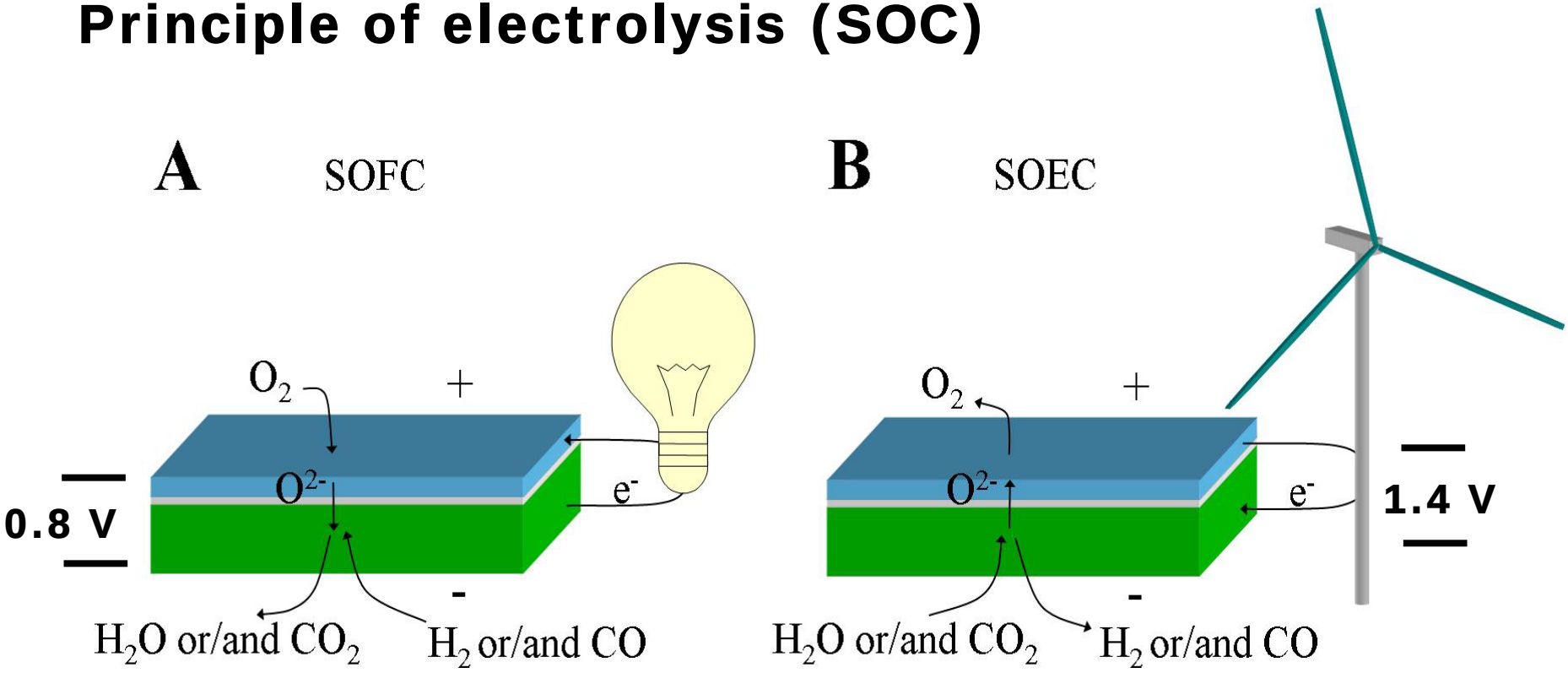
Electrolysis is needed

- Many technical principles are pointed out as suitable for storage technologies:
  - Pumping of water to high altitudes
  - Batteries
  - Superconductor coil (magnetic storage)
  - Flywheels
  - Electrolysis
  - Thermo-chemical looping
  - Solar Thermal Electrochemical
  - Photo-electrochemical HER and CO_2 reduction

- All are very important! But: first 4 are not for long distance (> 500 km) transport. 3 last are early stage research - may prove efficient in the future.

- Therefore, within a foreseeable future: **Electrolysis is necessary in order to get enough renewable fuels!**

Principle of electrolysis (SOC)



750 - 850 °C **EMF ca. 1.1 V**

Working principle of a reversible Solid Oxide Cell (SOC). The cell can be operated as a SOFC (A) and as a SOEC (B).

Production of syngas (SOEC case)

Reaction Schemes:

The overall reaction for the electrolysis of steam plus CO_2 is:

$$H_2O + CO_2 + \text{heat} + \text{electricity} \rightarrow H_2 + CO + O_2 \quad (1)$$

This is composed of three partial reactions. At the negative electrode:

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \quad (2)$$

$$CO_2 + 2e^- \rightarrow CO + O^{2-} \quad (3)$$

and at the positive electrode:

$$2\ O^{2-} \rightarrow O_2 + 4e^- \quad (4)$$

Production of syngas (from H_2 and CO_2)

The water-gas shift (WGS) reaction:

$$CO_2 + 2\ H_2 \leftrightarrows CO + H_2 + H_2O$$

By condensation of the water pure syngas is obtained

From syngas all kinds of hydrocarbons and alcohols can be produced by commercial available catalytic reactors – Methanol and methane syntheses, Fisher-Tropsch +++

Why synthetic hydrocarbons? The energy density argument

Comparison of Energy Storage Types. Only the batteries are including containers.

Storage type	MJ/L	MJ/kg	Boiling point, °C
Gasoline	33	46	40 – 200
Dimethyl ether - DME	22	30	- 25
Liquid methane	24	56	-162
Liquid hydrogen	10	141	-253
Compressed air – 20 MPa	0.1	0.4	
Water at 100 m elevation	10^{-3}	10^{-3}	
Lead acid batteries	0.4	0.15	
Li-ion batteries	1	0.5	

Why synthetic fuel?
The power density argument

- Gasoline filling rate of 20 L/min equivalents 11 MW of power and means it takes 2½ min to get 50 l = 1650 MJ on board

- For comparison: Li-batteries usually requires 8 h to get recharged. For a 300 kg battery package (0.5 MJ/kg) this means a power of ca. 3.5 kW i.e. it takes 8 h to get 150 MJ on board.

- The ratio between their driving ranges is only ca. 5, because the battery-electric-engine has an efficiency of ca. 70 % - the gasoline engine has ca. 25 %.

Visions for synfuels from electrolysis of steam and carbon dioxide

1. **Big off-shore wind turbine parks coupled to a large SOEC – produce CH_4 (synthetic natural gas, SNG) - feed into existing natural gas net-work (in Denmark).**

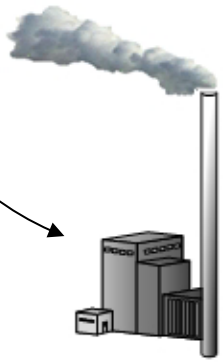
2. **Large SOEC systems - produce DME, gasoline and diesel - Iceland, Canada, Greenland, Argentina, Australia … geothermal, hydro, solar and wind.**

3. **Target market: replacement of natural gas and liquid fuels for transportation**

4. **All the infrastructure exists!!**

Vision, Biomass CO_2 recycling

Short term realisation - CO_2 capture from industrial sources



CO_2
Released to the atmosphere

H_2O
Released to the atmosphere

Synthetic petrol/diesel

Consumption

Fuel synthesis
$2\,H_2 + CO \rightarrow -CH_2- + H_2O$

Fuel transport

$CO + H_2$

Electrolysis cell
$2H_2O \rightarrow 2H_2 + O_2$
$2CO_2 \rightarrow 2CO + O_2$

$2O^{2-}$

÷

+

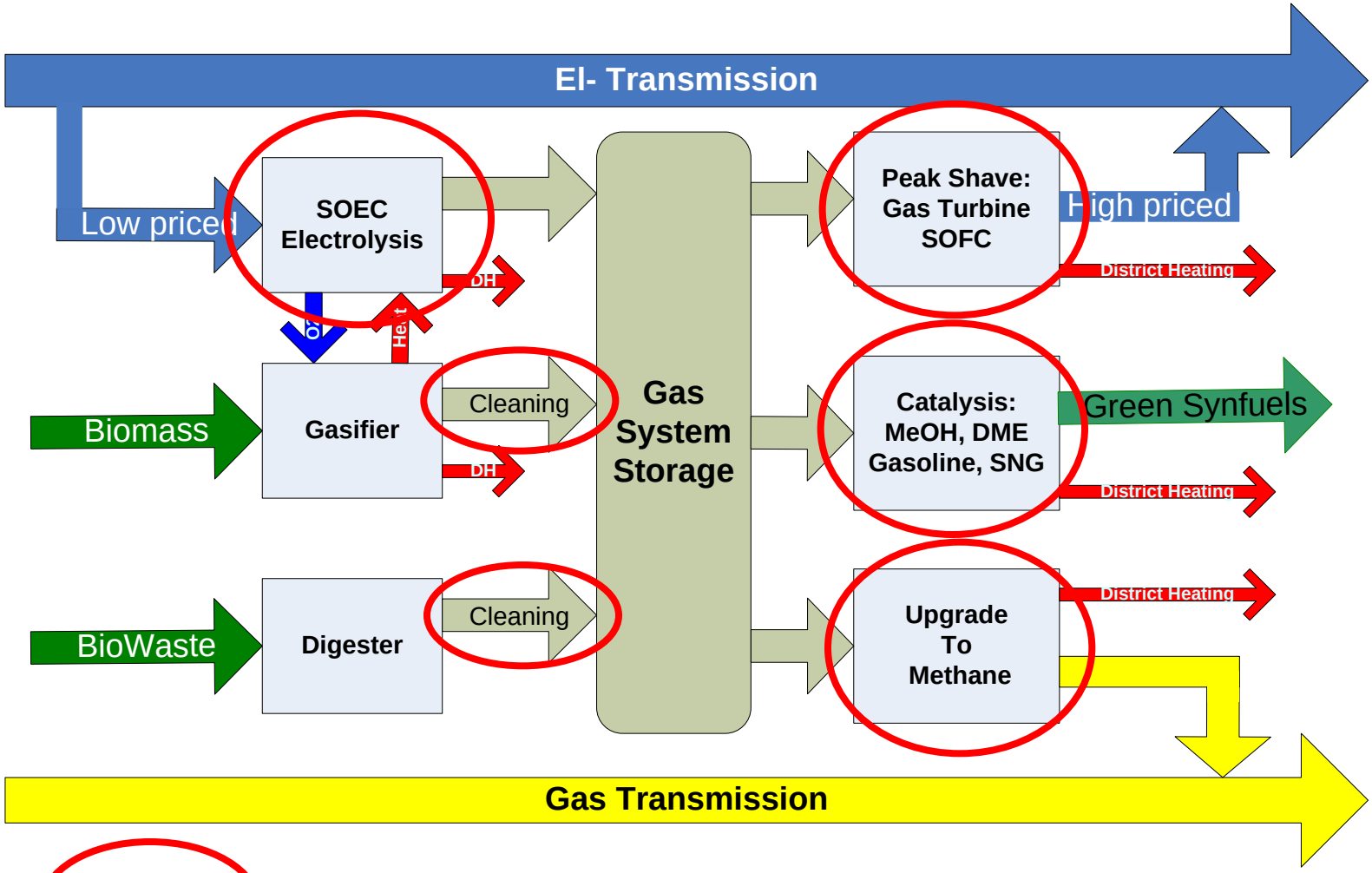
4 e⁻

(Renewable) Electricity

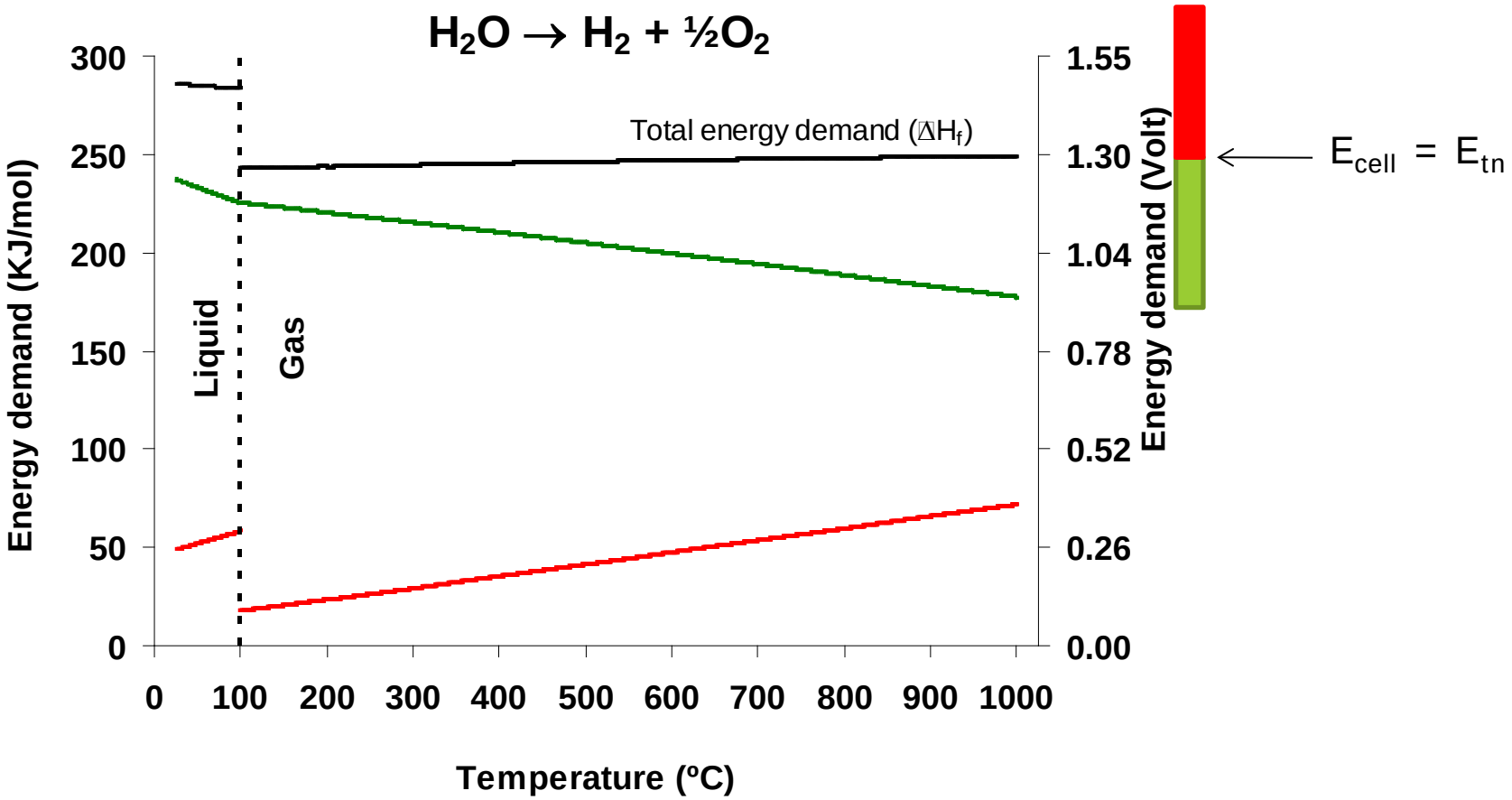
Concentrated CO_2

H_2O

Energinet.dk's vision for fossil fuel free Denmark in 2050 – The Wind Scenario



Thermodynamics



Energy ("volt") = Energy (kJ/mol)/2F

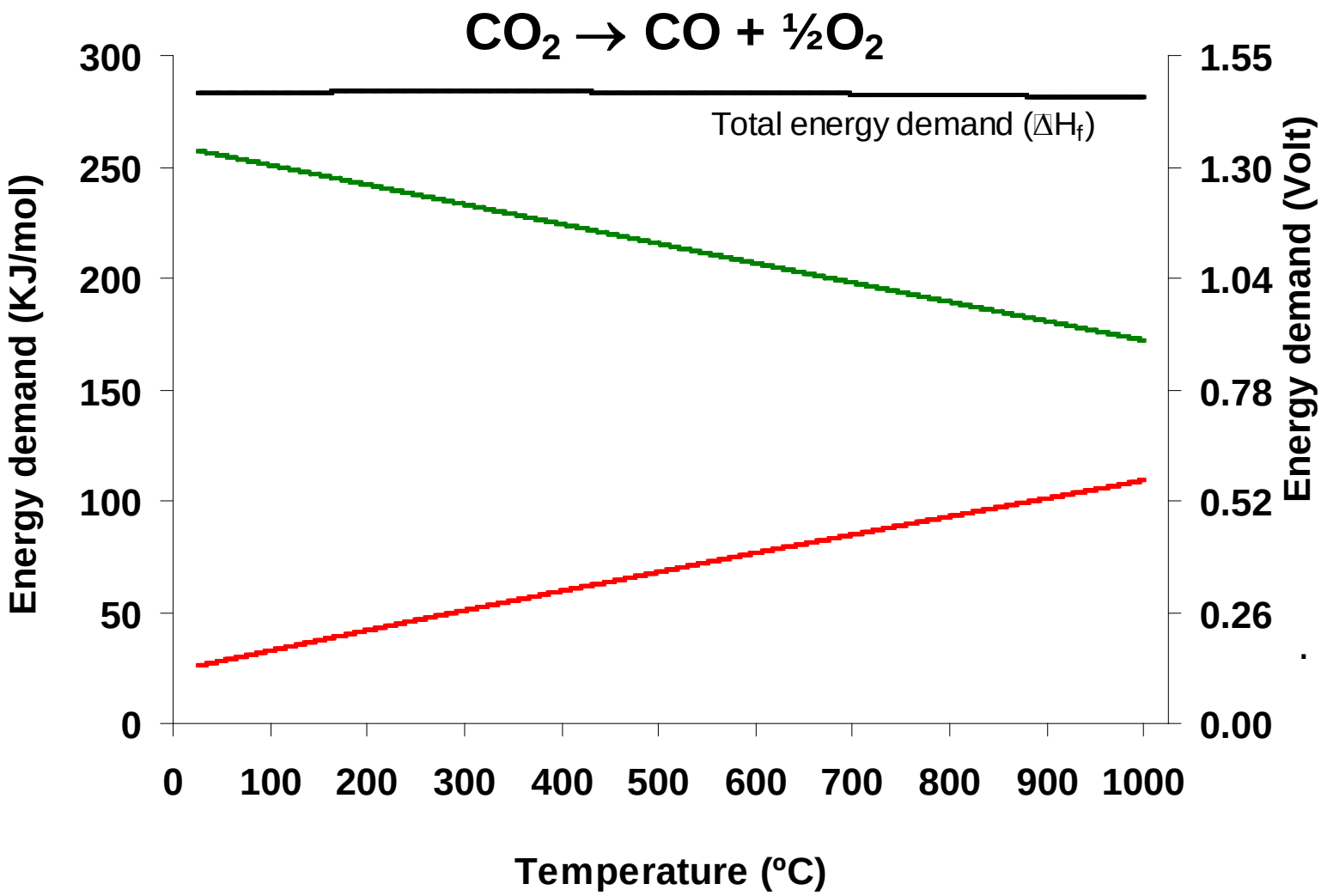
$E_{tn} = \Delta H/2F$

$i \propto E_{cell} - \Delta G/2F$

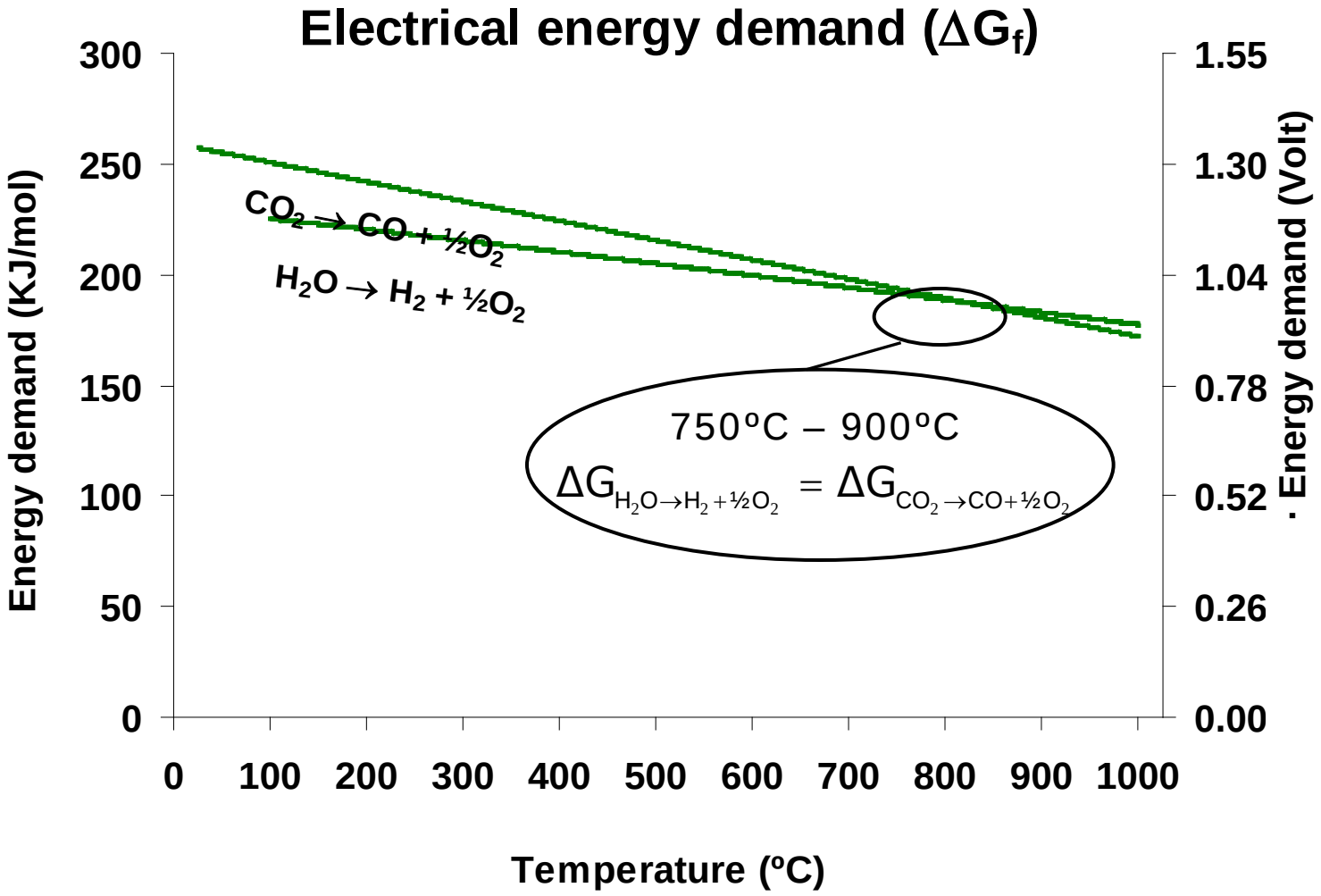
Price $\propto 1/i$ $[A/cm^2]$,

$\Delta H/\Delta G > 1$, $\eta = 100\,\%$ at $E = E_{tn}$ (no heat loss)

Thermodynamics



Thermodynamics: CO_2 and H_2O



Electrolysis and Fuel Cell Types

1. Simple aqueous electrolytes (e.g. KOH or K_2CO_3), room temperature to ca. 100 °C, 0.1 - 3 MPa pressure. The classic versions of alkaline electrolyser and fuel cell are not directly reversible.

2. Low temperature “solid” proton conductor membrane (PEM), 60 – 80 °C, and high temperature PEM 120 - 190 °C. Not directly reversible

3. Immobilized aqueous K_2CO_3, Na_2CO_3 KOH in mesoporous structures, solid acids etc. – pressurized 200 – 300 °C, 0.3 – 10 MPa. Probably directly reversible.

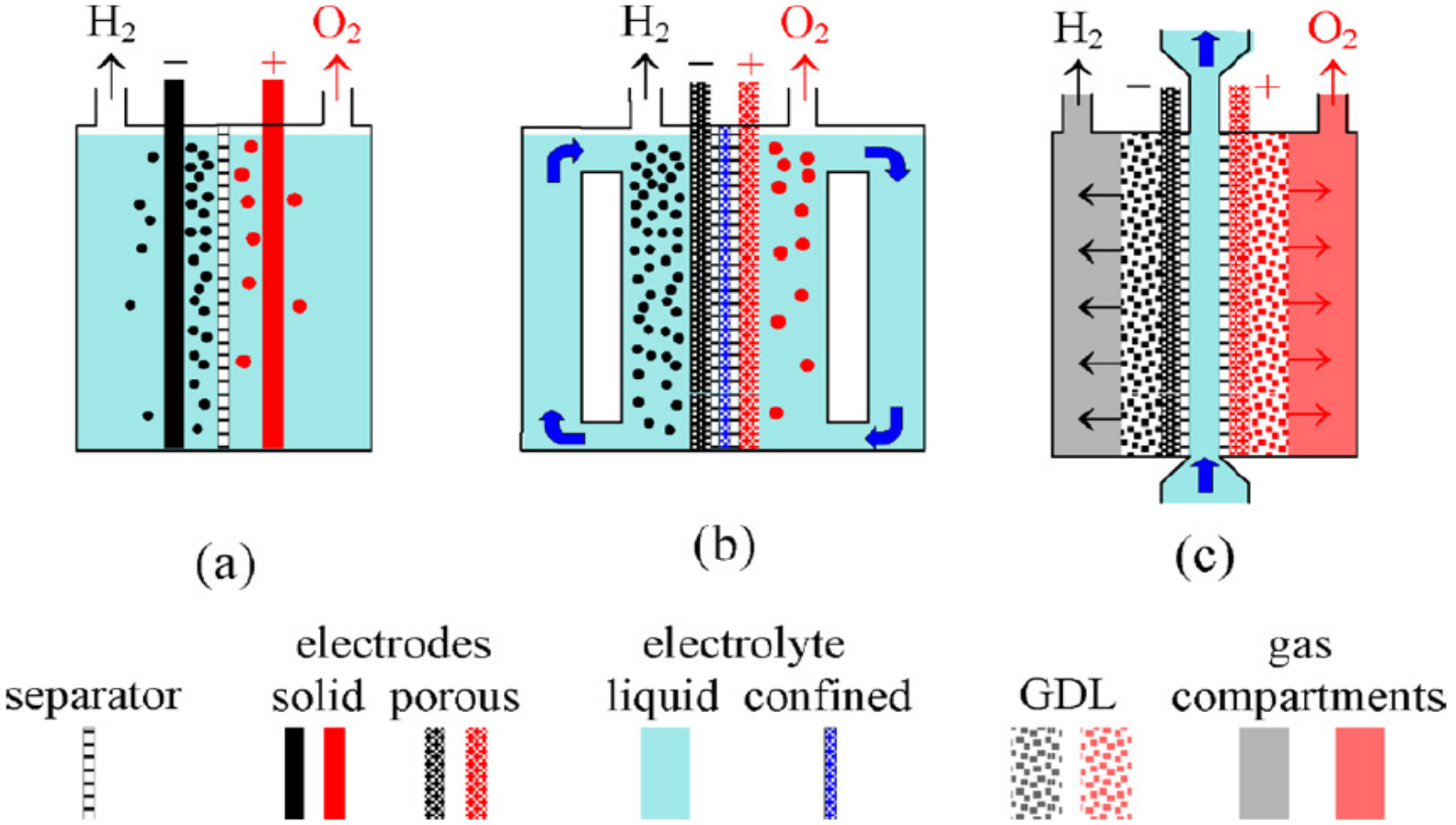
4. Molten carbonate electrolytes, fuel cells 650 °C; electrolyser 800 – 950 °C, 0.1 MPa. Electrolytes have different compositions, so not directly reversible. Only CO_2 electrolysis.

5. High temperature solid oxide ion conductor (stabilized zirconia), 650 – 950 °C, pressurized 0.5 – 2 (5?) MPa. Reversible!

Alkaline Electrolysis cells: Principles - reactions

- The electrolyte is usually ca. 30 wt% KOH in water
- Cathode (negative electrode) reaction:
  $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$
- Anode (positive electrode) reaction: 2
  $OH^- \rightarrow ½\ O_2 + H_2O + 2\ e^-$
- Total: $H_2O \rightarrow H_2 + ½\ O_2$
- Very simple reaction, which may be carried out in practise at a temperature as low as 60 °C
- Even so, it shows up that systems are not that simple

Principle designs

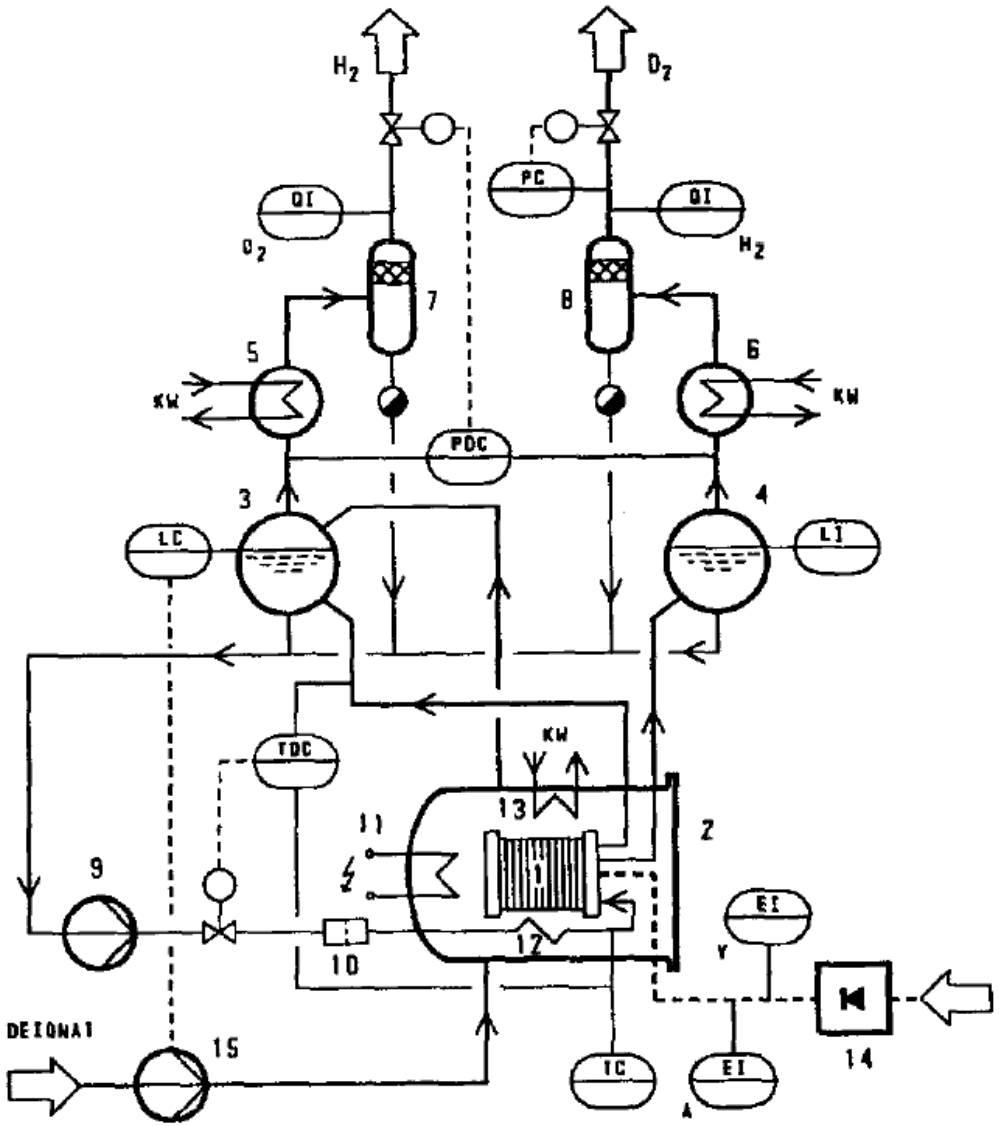


Different architectures of electrolyzers with: (a) immersion electrodes, (b) porous electrodes in the "zero-gap" configuration, (c) electrodes comprising Gas Diffusion Layers (GDL) separating the gas compartments and the re-circulating electrolyte compartment. From: S. Marini et al., Electrochimica Acta, **82** (2012) 384

Process flow diagram of a modern electrolyzer

1 Electrolytic cells
2 Electrolyzer pressure vessel
3 Hydrogen-electrolyte separator
4 Oxygen-electrolyte separator
5 Hydrogen cooler
6 Oxygen cooler
7 / 8 Condensate separators
9 Electrolyte circulating pump
10 Electrolyte filter
11 Electric heater
12 Electrolyte heater/cooler
13 Water cooler
14 Rectifier unit
15 Electrolyte feed pump

In principle reversible, but not in practice



Hydrogenics Alkaline system

From Hydrogenics' homepage:

HySTAT® 10 – 10

10 Nm^3H_2 h^{-1}, 5.4 kWh/Nm^3 H_2

PEM

- The main advantage of polymer membrane fuel cell and electrolyser cell is that it is compact and operates at 60 – 80 C, making the balance of plant relatively inexpensive.

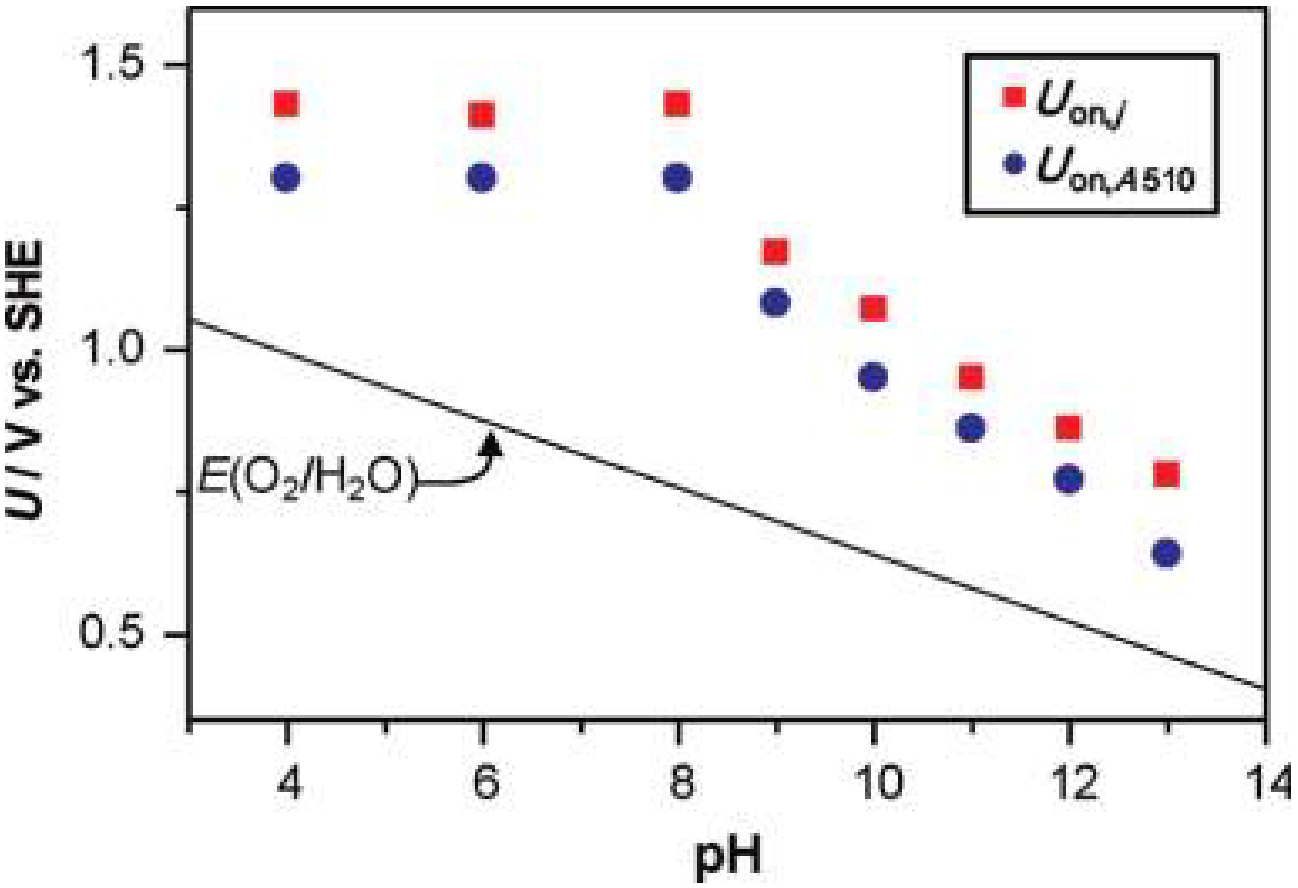
- Main problem is cost of cell and stack materials, in particular in case of the electrolyser.

- The oxygen electrode cannot use the carbon support used in the PEMFC – Ti alloys instead. The usual PEMFC degrades very fast if used in electrolyser mode.

A PEM problem: Electrocatalysis

- It is well-known that both H_2 and O_2 electrodes are very sluggish at temperatures below 100 °C and not fast until above 200 °C in particular in acid electrolytes.
- However, a lot of confusing data have been reported
- O_2 evolution as a function of pH as example

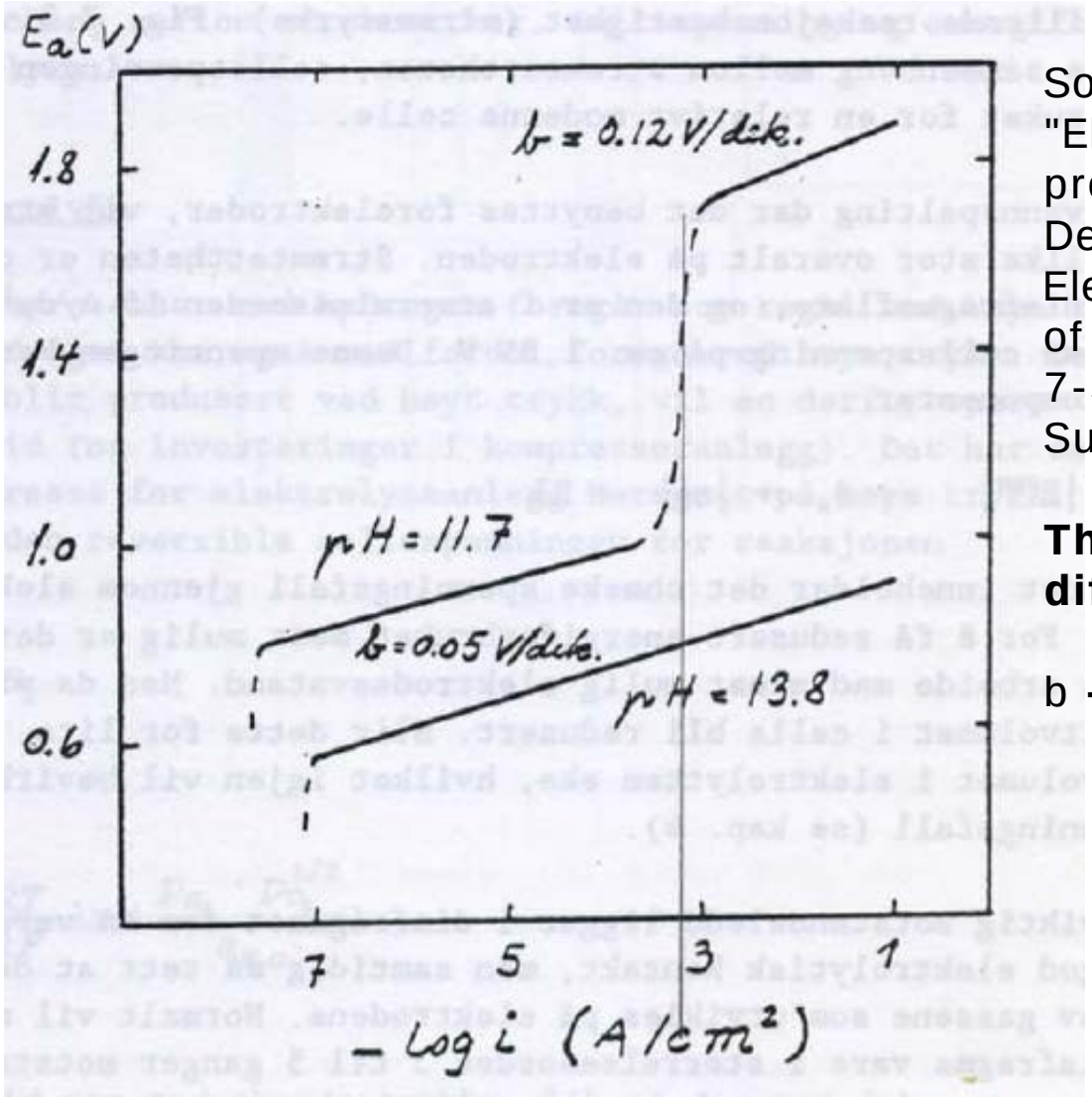
Oxygen evolution vs pH on MnO_x



$U_{on,j}$ is the onset potential of the OER in mixtures of aqueous NaOH and H_2SO_4 at 30 °C. $U_{on,A510}$ is the onset of the optical spectral line of Mn^{3+} on electrode surface taken as a (probably false) indication of Mn^{3+} being efficient electrocatalyst.

From: T. Takashima et al., Mechanisms of pH-Dependent Activity for Water Oxidation to Molecular Oxygen by MnO_2 Electrocatalysts, J. Am. Chem. Soc., 2012, **134**, 1519

Oxygen evolution vs pH



Source: Jomar Thonstad: "Elektrolyseprosesser/Electrolysis processes", Lecture notes, Department of Industrial Electrochemistry, Norwegian Institute of Technology (NTH/NTNU) (1991) p. 7-5A. Provided to me by Svein Sunde, NTNU, April 2013.

The vertical line indicates a diffusion limiting current density.

b **– values are Tafel slopes**

Oxygen evolution vs pH

The NTNU data is interpreted as follows:

The diffusion limited species is OH^-

At low current density or high pH the OER is reduction of OH^-:

$2\ OH^- \rightarrow ½\ O_2 + H_2O + 2\ e^-$

At high current density (above the OH^- limiting diffusion rate) or low pH the OER is reduction of H_2O:

$H_2O \rightarrow ½\ O_2 + 2\ H^+ + 2\ e^-$

It seems much easier to oxidize OH^- than H_2O

The correlation between OER overpotential and Mn^{3+} concentration was probably incidental approximate parallel oxidation reactions

Materials

- Thus, for acid cell like Nafion - PEM only the super electrocatalyst IrO_2 (and possibly RuO_2) are usable for oxygen evolution (electrolysis) and Pt for oxygen reduction and hydrogen oxidation (fuel cell)

- These and other of the cell and stack materials make the type far too expensive.

- As there are very clear technical advantages of the PEM type, inexpensive, high performance and durable PEM should be developed. Is under way. R&D of alkaline membrane cells are on-going.

- Increasing the temperature may also solve the problem.

New 200 – 300 °C cell types

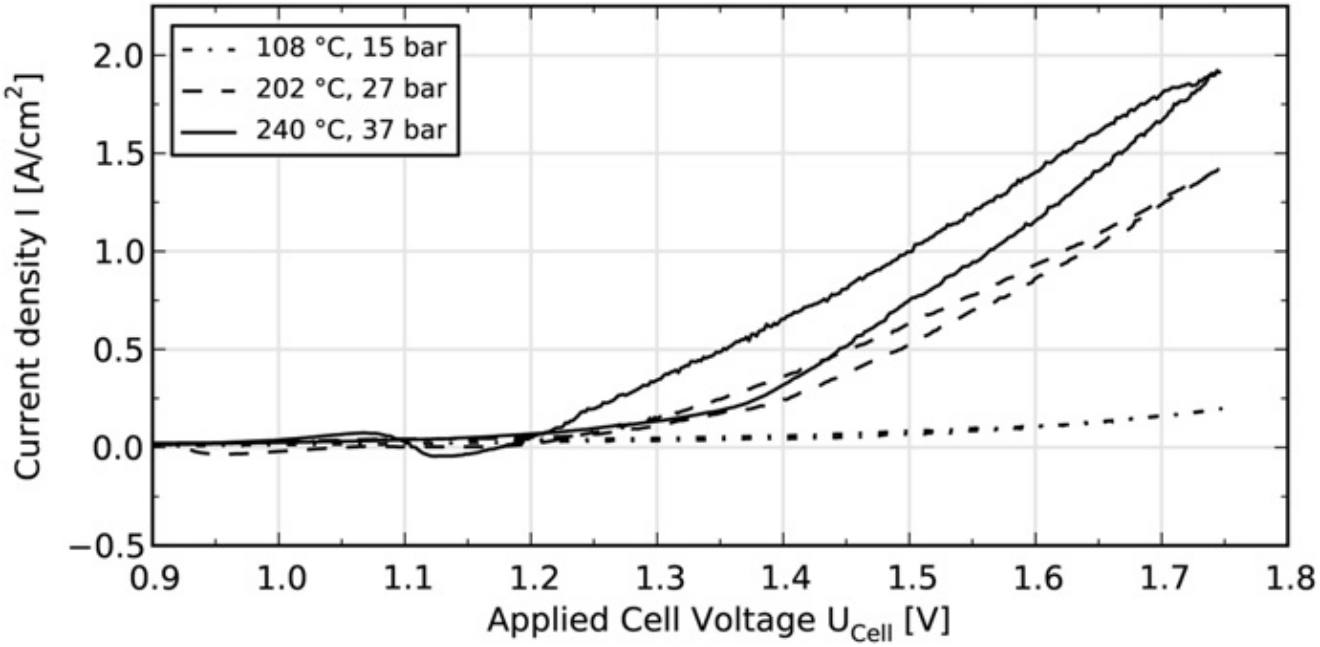
As part of the initiative called Catalysis for Sustainable Energy (CASE, www.case.dtu.dk) other types of electrolysis cells are being researched and developed at DTU Risø Campus.

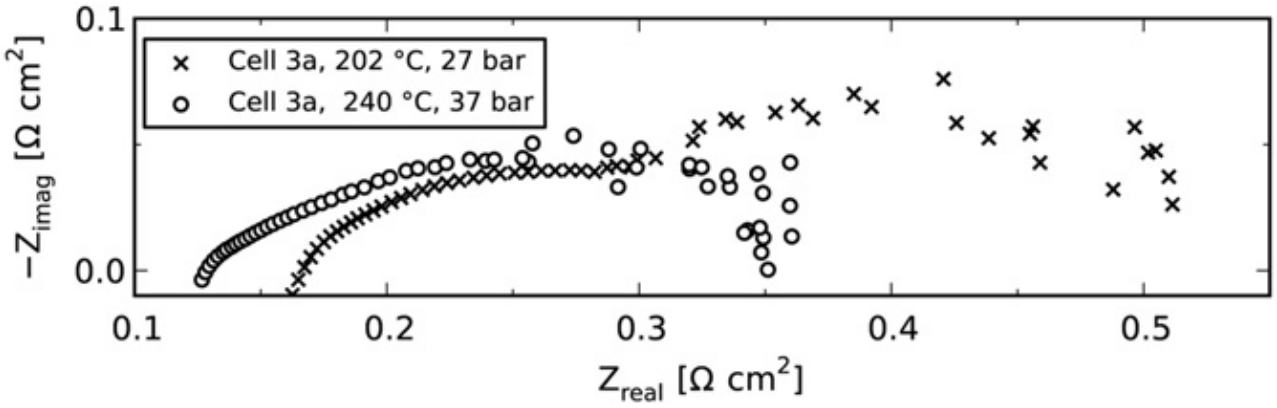
- Solid Acids (CsH_2PO_4)
- Immobilized aqueous K_2CO_3
- Immobilized aqueous KOH

This temperature range seems to be catching interest now, e.g. project work on similar is presented at this conference in a poster:

Andrej Latric et al., P049, "Methanol Steam Reformer – High Temperature PEM Fuel Cell System Analysis". High Temperature was given as 250 °C.

High Temperature in Alkaline Electrolysis

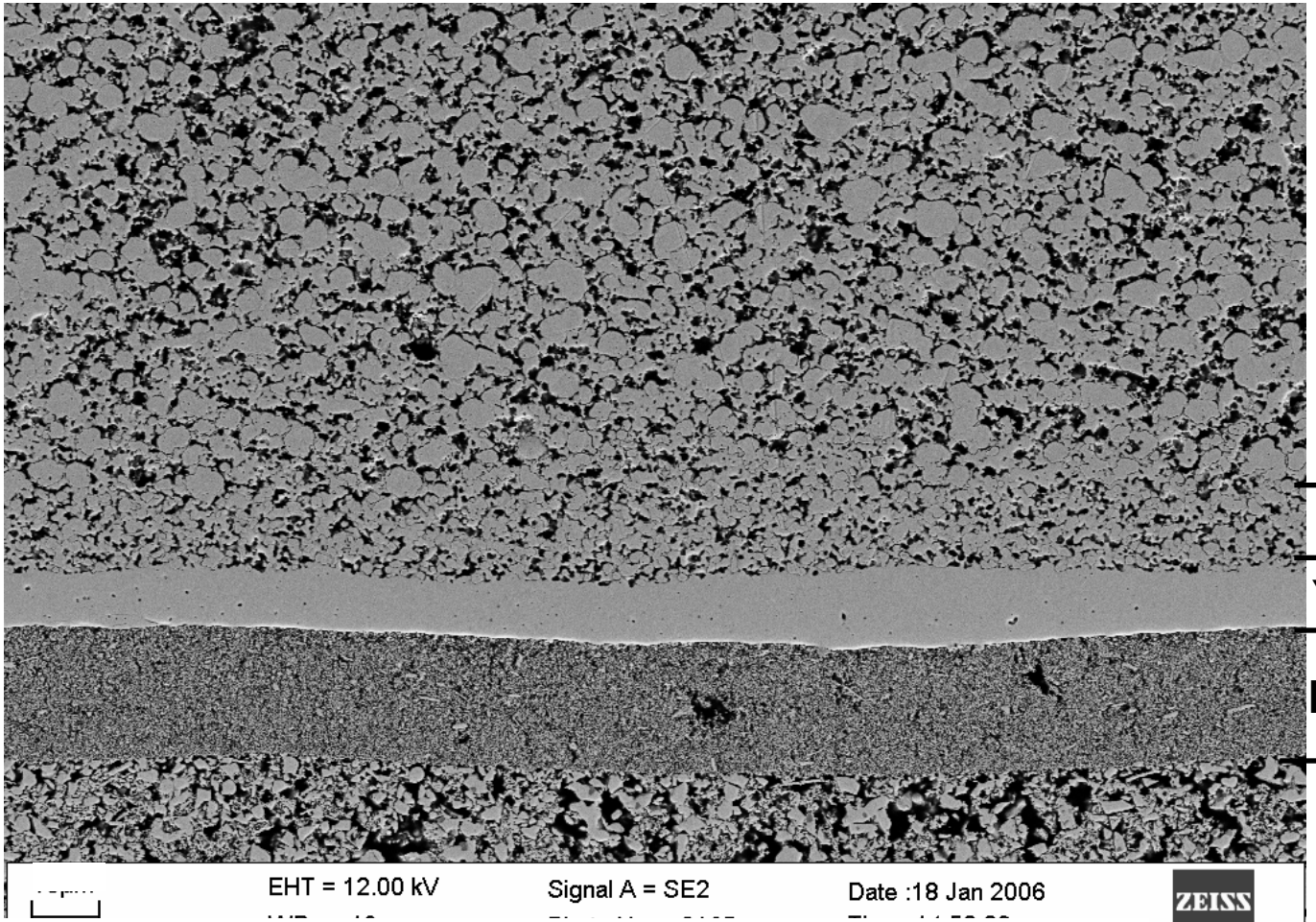




Cells with 45 wt% KOH (aq.) immobilized in mesoporous ceramic membrane (electrolyte) and with gas diffusion electrodes. Cathode: Inconel. Anode Ag deposited on Ni.

From: Allebrod, Chatzichristodoulou, Mogensen, J. Power Sources **229** (2013) 22

Ni-YSZ supported SOC



Ni / YSZ support

Ni / YSZ electrode

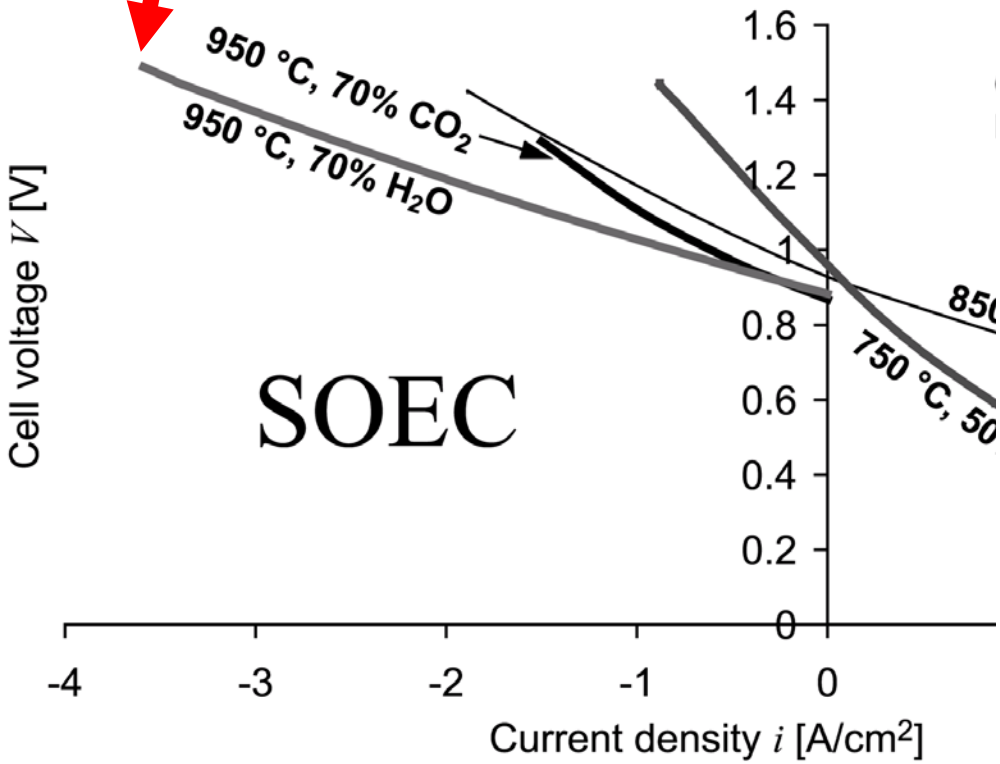
YSZ electrolyte

LSM-YSZ electrode

10 μm Acc. voltage: 12 kV SE image

SOEC Cell performance

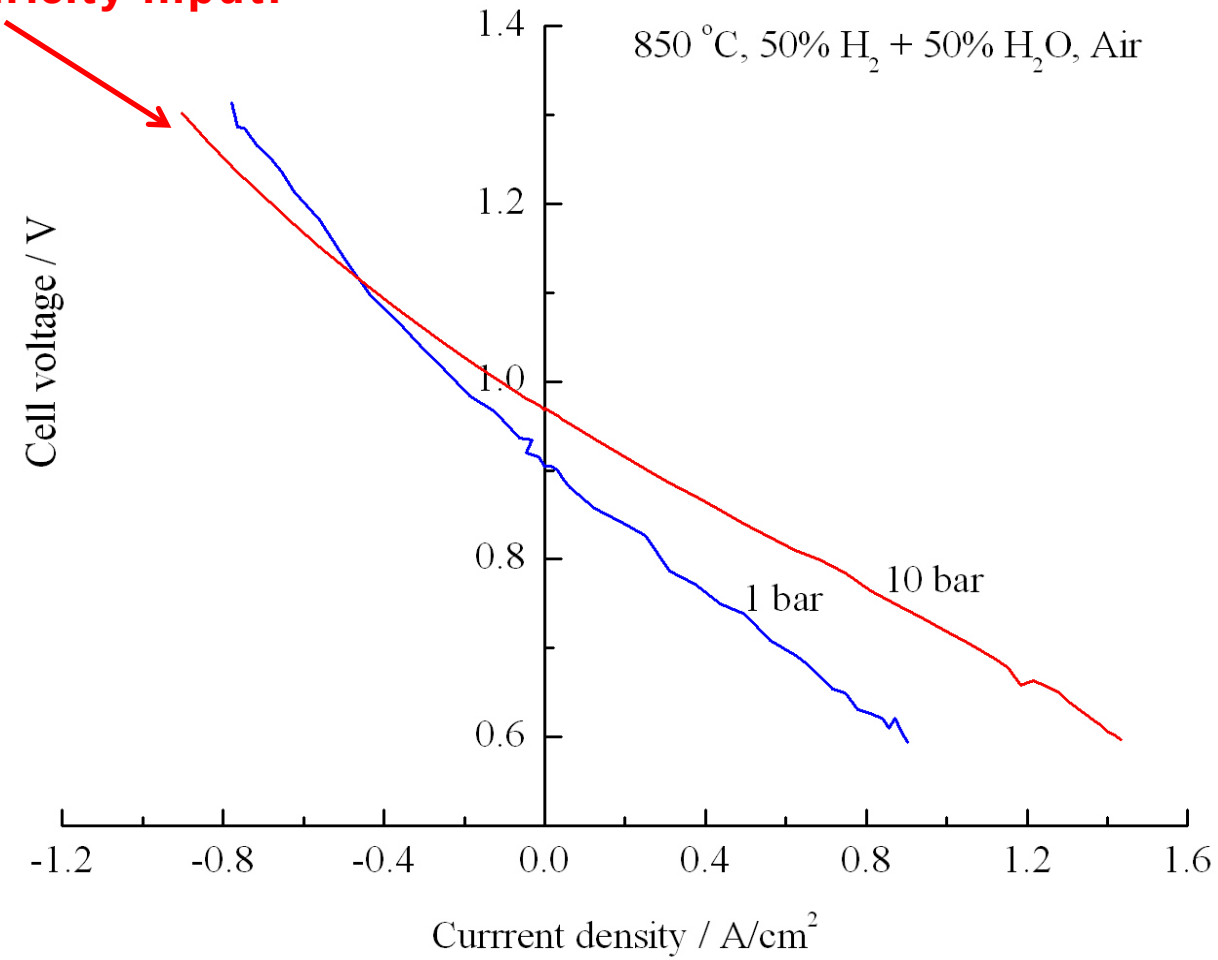
World record !



***i - V* curves for a Ni-YSZ-supported Ni/YSZ/LSM SOC: electrolyzer (negative current density) and fuel cell (positive current density) at different temperatures and steam or CO_2 partial pressures - balance is H_2 or CO.** **S.H. Jensen et al.,** International Journal of Hydrogen Energy, **32** (2007) 3253

SOEC Effect of pressure

We get pressurized hydrogen with lower electricity input!



SOC is being improved significantly

- The above results were from “old fashion” SOC with LSM electrodes and 10 micron electrolyte with ASR of 0.22 Ω cm² at 850 °C
- Much improved cells have been reported since, see literature from FZ-Jülich, KIT, DTU Risø, The Wachsman group in US, e.g. the FZ-J/KIT paper: F. Han et al., J. Power Sources, 218 (2012) 157. Their best cell was about 0. 1 Ω cm² at 750 °C in electrolyser mode
- These super results have yet to be implemented in stacks and tests also in electrolysis mode

Cell type status

- Few types commercialized but - from an energy conversion and storage point of view - none of them are commercial in today's energy markets.

- The classical alkaline electrolyser was commercialized during the first half of the 20th century and is closest to market today, but still too expensive.

- If significant amounts of synfuel via electrolysis in the very near future (the next 1 -5 years) – only the classical alkaline electrolysers is available on some scale – but still relatively limited.

- SOFC clearly has a vey high potential as reversible fuel cell – electrolyser cell in the future

Concluding Remarks

- In order to fulfill the visions we need to produce at least H_2 by electrolysis and possibly CO
- We need to capture and purify CO_2 from suitable sources
- Both above point may technically be done by several technologies – but the economy is yet problematic for all of them
- Energy efficiency is important for costs but not important in itself. The energy price for the consumer is the only important factor!
- The most economic SOC electrolysis – fuel cell cycle-efficiency may be (for the time being) only 40 %. Most of the round-trip-loss is in the fuel cell (heat "loss"). Possibly, it may be improved to 70 % with further R&D.
- Efficiency of conversion of fossil fuel in a car ca. 25 % and in a power plant usually below 40 % in average

There is a lot more to do

Research on all types should be done.

Demonstrations are necessary when new technology is being developed.

However, how big is the need for demonstration technology, where we know that the problems are far from solved yet?

Do we have the right balance between R&D on the one hand and Demonstrations on the other hand?

I think that spending much more money on fundamental applied research that can give a solid basis for further developments and then demonstrations would be a wise strategy

Thank you for your attention

Acknowledgements

I acknowledge support from our sponsors

- Danish Energy Authority
- Energinet.dk
- EU
- Topsoe Fuel Cell A/S
- Danish Programme Committee for Energy and Environment
- Danish Programme Committee for Nano Science and Technology, Biotechnology and IT
- The work of many colleagues over the years